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Effects of applied pressure in ZnV_2O_4 and evidences for a dimerized structure

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The series of V spinels $[A^{2+}]\ V_2\ O_4$ (A = Cd, Mn, Zn, Mg) provides an opportunity to tune the V-V distance continuously, in the frustrated pyrochlore lattice of the spinel. This system has been shown to approach the metallic state when V-V distance is reduced. The proximity to the transition leads to a dimerized structure in $ZnV_2\ O_4$ caused by lattice instabilities. A different manner to tune the V − V distance of this structure is to fix the A^{2+} cation (in our case, Zn) and apply pressure. We have analyzed the evolution of the electronic structure of the system in the dimerized state. Such structure prevents the system to present a metallic phase at moderate pressures. We have also calculated the transport properties in a semiclassical approach based on Boltzmann transport theory. Our results support the validity of this structural distortion by providing a nice fit with experimental measurements. © *2011 American Institute of Physics*. [doi:10.1063/1.3565410]

I. INTRODUCTION AND COMPUTATIONAL DETAILS

The series of oxide spinels $AV_2\ O_4$ (A = Cd, Mn, Zn or Mg), that presents a frustrated pyrochlore lattice for V cations, approaches an insulator-metal (Mott) transition when the V − V distance is reduced sufficiently, by applying pressure or by changing the size of the A^{2+} cation.[1,2] $ZnV_2\ O_4$ is the closest member of the series to the metallic state.

The ground state of the spinel compounds has produced an intense theoretical research in the last years.[3–7] The tetragonal distortion at $T_S = 51K$ produces the t_{2g} levels split into a lower d_{xy} level and twofold degenerate d_{xz} and d_{yz} level. It is clear that the first electron of V^{3+}: d^2 occupies entirely the d_{xy} level, whereas the second one is located in a combination of the other t_{2g} -orbitals d_{xz} and d_{yz}.[8]

Three main models try to solve this d_{xz} and d_{yz} occupations: the real orbital ordered model, where the ground state consists of alternating occupation of the d_{yz} or d_{xz} orbital in successive layers along the c axis;[3] the complex orbital order model where the second electron occupies the complex orbital $(d_{yz} \pm id_{xz})$ which has an unquenched value of the orbital angular momentum;[4] and a third model that takes into account the proximity of $ZnV_2\ O_4$ to the itinerant-electron boundary,[6] showing a dimerization along the V − V chains, which is described by the formation of homopolar molecular V − V bonds, characterized by a partial electronic delocalization (the orbital wave functions in this case would be a real combination of orbitals $(d_{yz} \pm d_{xz})$ with no net orbital moment).

In the present paper we will make an analysis of the effects of applied pressure in the dimerized structure of $ZnV_2\ O_4$ and analyze the importance of the structural distortion in preventing the occurrence of a pressure-induced metallization.

Full potential, all electron, electronic structure calculations have been performed within density functional theory[9] using WIEN2k software,[10,11] which utilizes an augmented plane wave plus local orbitals (APW + lo)[12] method. The exchange-correlation potential utilized was the Perdew, Burke, and Ernzerhof (PBE) version of the general gradient approximation (GGA).[13] The geometry optimization was carried out minimizing the forces in the atoms and the total energy of the system to all the pressures calculated in this work. We converged with respect to the k-mesh and to $R_{\mathrm{mt}}K_{\max}$. We have used a 6 × 6 × 4 sampling of the full Brillouin zone for electronic structure calculations and geometry optimization. $R_{\mathrm{mt}}K_{\max} = 7.0$ is chosen for all the calculations. Muffin-tin radii chosen were the following: 1.89 a.u. for Zn, 1.96 a.u. for V, and 1.68 a.u. for O.

For modeling the behavior of d electrons, we included strong correlation effects by means of the LDA + U scheme,[14] where the correlation effects are controlled by an effective U ($U_{\mathrm{eff}} = U - J$), being U the on-site Coulomb repulsion and J the on-site exchange constant (taken as $J = 0$, as is common practice in literature).[15] A value of $U_{\mathrm{eff}} = 3.0$ eV was used in the calculations. This value has been chosen because it reproduces the gap obtained experimentally by Pardo *et al.*[6] For the calculations of transport properties we utilized the BoltzTraP code,[16] that uses the energy bands obtained from the WIEN2k software. We used a 42 × 42 × 30 sampling of the full Brillouin zone, where convergence was achieved. The calculation of transport properties requires a fine mesh to carry out the integrations in the Brillouin zone.

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II. RESULTS AND DISCUSSIONS

The electronic structure of dimerized ZnV_2O_4 has been calculated recently.[17] The proximity to the transition causes lattice instabilities that lead to bond-length fluctuations that stabilize the formation of V − V molecular orbitals.

Some studies of the effects of chemical pressure in the series AV_2O_4 (Refs. 1 and 6) show that reduced V − V distance (from 3.07 Å for Cd^{2+} ion to 2.97 Å for Mg^{2+} ion) can drive these systems close to an insulator-metal transition. The critical distance for itineracy was estimated at about 2.94 Å,[18] attainable with a reasonably small pressure for the compounds with a smaller cation, like Mg^{2+} or Zn^{2+}.

The nondimerized structure of MgV_2O_4 was studied *ab initio* previously.[2] This structure is close to the critical distance predicted experimentally for an insulator-metal transition. Applying pressure produces the transition (above $P = 6.5$ GPa in the nondimerized structure of MgV_2O_4). ZnV_2O_4 should present a similar behavior, due to the almost identical size between Mg^{2+} and Zn^{2+} cations (leading to a very similar V − V distance).

Testing this possibility in the dimerized structure found for ZnV_2O_4 was the main goal of the current work. In Fig. 1, we present the density of states (DOS) plots of the dimerized structure of ZnV_2O_4 at low ($P = 0.8$ GPa) and high ($P = 18.2$ GPa) applied pressure. The value of the gap at low pressure was obtained experimentally from resistivity measurements by V. Pardo *et al.*,[6] giving a value of ≈ 1.1 eV. At $P = 0.8$ GPa [Fig. 1 (a)] with $U = 3$ eV the material is an insulator with a bandgap of approximately 1.0 eV, reproducing very nicely the experimental gap.[6] The electronic structure of a Mott−Hubbard insulator with a *d-d* gap can be observed in the plot, where the V *d* character contribution near the highest lying occupied states and lower unocuppied states dominates (O *p* levels have less contribution in these energy ranges, but non-negligible).

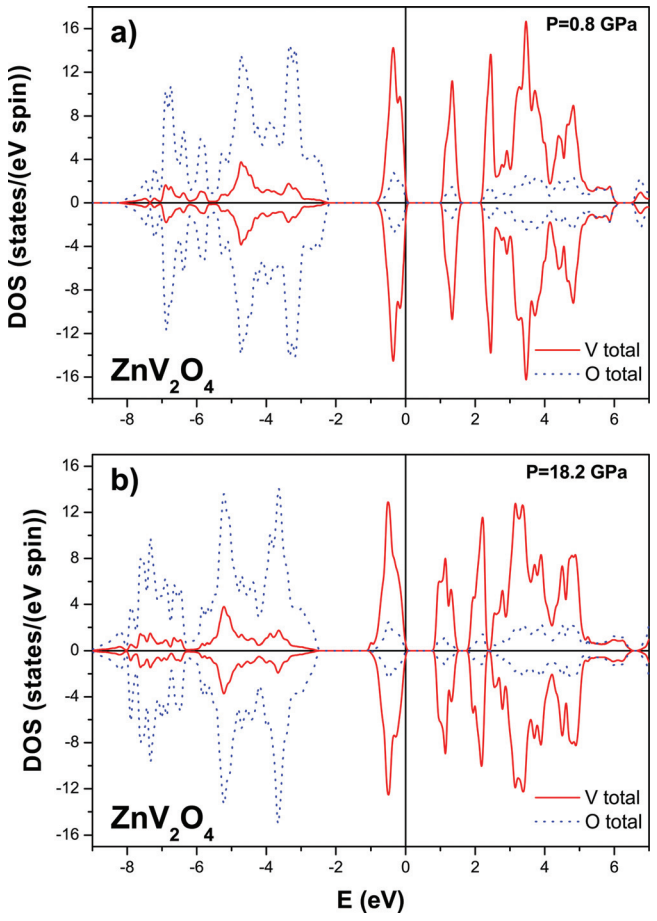

FIG. 1. (Color online) DOS plots for all the V and O levels in the unit cell for the dimerized structure at (a) $P = 0.8$ GPa and (b) $P = 18.2$ GPa. The *d-d* character of the narrow gap of 1.0 eV can be noticed in the low pressure density of states (a). A reduction of the gap to 0.8 eV can be noticed in the high pressure DOS (b), leading to a nonmetallized state. Upper (lower) panels show the spin-up (down) channel. Fermi energy is at zero.

Figure 1(b) still shows an insulating character of ZnV_2O_4 at $P = 18.2$ GPa in the dimerized state. The V − V distance is reduced to 2.84 Å in the short V − V bond and 2.95 Å in the long V − V bond (the shorter one would be well below the critical value for itineracy). While the nondimerized structure of MgV_2O_4 becomes metallic when pressure is applied, the dimerized state in ZnV_2O_4 does not allow metallization to occur. In this geometry, the system remains a Mott−Hubbard insulator. If we analyze the evolution of the gap in the dimerized structure at various pressures (Fig. 2) we observe a slow reduction of the gap, which would only predict a metallized state at very high pressures (above 100 GPa). The dimerized structure of ZnV_2O_4 prevents the metal-insulator transition to occur, as it would happen in the nondimerized structure. A pressure-induced metallic phase is not obtained for ZnV_2O_4. The reason for this behavior is the additional gap produced by the dimerization of the V − V chains along the [011] and [101] directions of the spinel structure. Further experimental evidence has been found very recently in favor of the dimerized structure,[19] with the observation of electrical polarization coexistent with the magnetically ordered phase, consistent with the appearance of dimerized chains in ZnV_2O_4.

We have also calculated the thermoelectric power evolution with temperature and have compare it with experimental data. Taking the conductivity (σ) and Seebeck coefficient (S) calculated from spin-up and spin-dn channels, the total

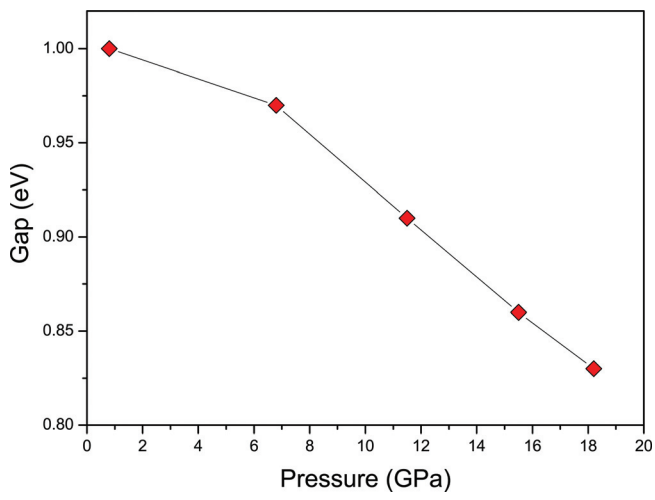

FIG. 2. (Color online) Gap evolution with pressure in the dimerized state of ZnV_2O_4. The line is just a guide for the eye.

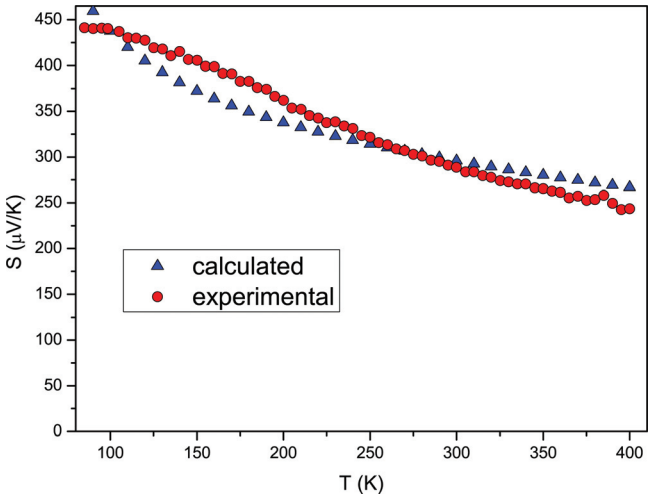

FIG. 3. (Color online) Experimental and calculated temperature dependence of the thermopower.

thermopower is obtained according to the two-current model[20] expression:

$$S = \frac{\sigma'(\uparrow)S(\uparrow) + \sigma'(\downarrow)S(\downarrow)}{\sigma'(\uparrow) + \sigma'(\downarrow)}, \quad (1)$$

where $\sigma' = \sigma/\tau$, in the constant relaxation time approximation. We present both the calculated data and the experimental values of the Seebeck coefficient (taken from Ref. 1) in Fig. 3. The calculated values are in good agreement with the experimental ones. The approximately linear Seebeck coefficient (compared with the values of thermopower of other compounds of the AV_2O_4) is consistent with the material being close to a metal-insulator transition, away from the standard activated behavior found in the more insulating isoelectronic compounds.[1] This gives further evidence for the validity of our description of the dimerized compound.

To summarize, we have analyzed the electronic structure of the oxide spinel ZnV_2O_4: We have studied the effect of applying pressure on the compound in the dimerized structure and have observed a Mott–Hubbard insulating character at high pressure. The dimerization of the V – V chains in the spinel structure, produced by the proximity to a metal-insulator transition, prevents the system to reach a fully metallic state. We have also calculated the thermopower of this Zn dimerized spinel and have compared it with experimental measurements. Calculated Seebeck coefficient of the dimerized structure shows a linear (nonactivated) behavior, and fits nicely with experimental measurements. This provides additional support to our description of the lattice distortions that occur in ZnV_2O_4 close to the metallic state.

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